

Crystal Structures, Characterizations and Fluorescence Properties of Two 3D Ca(II)/Sr(II) Coordination Polymers Based on 2-Sulfoterephthalate

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ABSTRACT Two alkaline earth metal coordination polymers [M(2-Hstp)(H₂O)] (M = Ca²⁺ (**1**) and Sr²⁺ (**2**), 2-H₃stp = 2-sulfoterephthalate) were synthesized under hydrothermal conditions by the precursor [Mn(2-Hstp)₂(4,4'-Hbpy)₂] and alkaline earth metal salts. The two alkaline earth complexes are not isomorphic. Complex **1** crystallizes in the monoclinic space group *P*2₁/*m*, while **2** in the monoclinic space group *P*2₁/*c*, despite of their similar formulas. In **1**, the Ca²⁺ ion lies in a seven-coordinated pentagon bipyramidal configuration, coordinated with five 2-Hstp²⁻ anions and one water molecule. However, the Sr²⁺ ion in **2** is coordinated by nine oxygen atoms to form a single-capped square antiprism polyhedron. Both **1** and **2** exhibit π - π^* emission of the 2-sulfoterephthalate ligand.

Keywords: alkaline earth metal complex; 2-sulfoterephthalate; crystal structure; luminescence property;

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1 INTRODUCTION

Metal-organic coordination polymers have been rapidly developed in the past decades due to their fascinating structures or topologies, especially their potential applications in catalysis, magnetism, gas storage, adsorption, luminescence, photoluminescence and so on^[1-7]. Many efforts have been devoted to selecting suitable ligands because they play a crucial role in the rational design of structures with specific physical and chemical properties^[8]. The organic ligands containing carboxylate have received considerable attention for the

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versatile binding modes as a bridging linker between inorganic moieties^[9, 10]. 2-Sulfoterephthalic acid has two carboxylate groups and one sulfonate group that can serve as bridging groups to form multi-dimensional coordination networks. Moreover, the adjacent 2-site sulfonate and 1-site carboxylate group favor stranded and helical structures, and some literatures have reported the *d*-block transitional metal complexes^[11-13]. Based on 2-sulfoterephthalate, we have designed and synthesized many metal-organic frameworks, including several lanthanide complexes and transitional metal complexes^[14-16].

Compared to *d*- and *f*-block metal ions, alkaline earth metals received much less attention^[17-19], because of the unpredictable coordination number and the tendency to form solvated metal centers^[20, 21]. Some *s*-block coordination complexes are already of commercial importance^[22], for instance, Tanay et al. synthesized three new alkaline earth metal (Ca, Sr, Ba) based coordination complexes with interesting structural diversity, variable chemical stability as well as proton conductivity^[23]; Debasis et al. reported a series of *s*-block coordination polymers with novel lightweight sensing materials^[24]; two Ba(II)-based and two Ca(II)-based 3D frameworks with high thermal stability and photoluminescent were synthesized by Shunfu Du et al. under similar reaction conditions and stoichiometry^[25]; and Dong Woo Lee et al. successfully synthesized and characterized a novel multifunctional non-centrosymmetric strontium-organic framework material with high thermal stability^[26].

It is still a tempting challenge to synthesize alkaline earth metal coordination polymers with attractive structures and applications. Herein, we obtained two 3D microporous complexes [M(2-Hstp)(H₂O)] (M = Ca and Sr) by exchanging the ions from the precursor [Mn(2-Hstp)₂(4,4'-Hbpy)₂] under hydrothermal conditions, and investigated their crystal structures and luminescence properties.

2 EXPERIMENTAL

2.1 Materials and methods

All chemicals and solvents were commercially available and used without further purification. Elemental analyses for C, H and N were carried out with a Vario EL elemental analyzer. The FT-IR spectra were recorded from KBr pellets in the range of 4,000~400 cm⁻¹ on a Nicolet Avatar 360 FT-IR spectrometer. Powder X-ray diffraction (PXRD) patterns were measured with a PANalytical X' Pert PRO MPD diffractometer (CuK α , λ = 1.5406 Å). Thermogravimetric analysis (TGA) was measured on a Mettler Toledo TGA/DSC

thermogravimetric analyzer (Switzerland) at a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ from room temperature to $900\text{ }^{\circ}\text{C}$ in the air. The fluorescence measurements were carried out with a F4500 spectrofluoro-photometer.

2.2 Synthesis

Preparation of the precursor $[\text{Mn}(\text{Hstp})_2(4,4'\text{-Hbpy})_2]$ The precursor complex $[\text{Mn}(\text{Hstp})_2(4,4'\text{-Hbpy})_2]$ was prepared according to the method of the literature^[14].

$[\text{Ca}(\text{2-Hstp})(\text{H}_2\text{O})]$ (1) A mixture containing the precursor $[\text{Mn}(\text{Hstp})_2(4,4'\text{-Hbpy})_2]$ (0.0085 g) and CaCl_2 (0.0020 g), isopropyl alcohol (0.5 mL) and H_2O (0.5 mL) was sealed in a 15 mL Teflon-lined autoclave and heated under autogenous pressure to $140\text{ }^{\circ}\text{C}$ for 96 h and then cooled to room temperature naturally. After filtration, some colorless crystals were collected, washed with ethanol, and dried in air (yield 49.5% based on Ca). Anal. Calcd. for $\text{C}_8\text{H}_6\text{CaO}_8\text{S}$ (302.27): C, 31.76; H, 1.98%. Found: C: 31.55; H: 2.14%. FT-IR (cm^{-1}): 3426 (s), 2908 (m), 2359 (w), 1690 (m), 1560 (m), 1422 (w), 1235 (s), 1100 (m), 767 (w), 664 (w), 618 (m), 533 (w).

$[\text{Sr}(\text{2-Hstp})(\text{H}_2\text{O})]$ (2) This compound was obtained analogously to compound **1** using $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ instead of CaCl_2 (yield 51.2% based on Sr). Anal. Calcd. for $\text{C}_8\text{H}_6\text{SrO}_8\text{S}$ (349.81): C, 27.43; H, 1.72%. Found: C: 27.05; H: 2.08%. FT-IR (cm^{-1}): 3422 (s), 2927 (w), 2359 (w), 1705 (m), 1578 (s), 1420 (m), 1185 (s), 1073 (m), 1024 (m), 771 (w), 655 (w), 610 (m), 526 (w), 457 (w).

2.3 Crystal structure determination

Single-crystal X-ray diffraction analyses of $[\text{M}(\text{2-Hstp})(\text{H}_2\text{O})]$ ($\text{M} = \text{Ca}^{2+}$ and Sr^{2+}) were recorded with a Bruker SMART APEX CCD diffractometer equipped with a graphite-monochromated $\text{MoK}\alpha$ radiation ($\lambda = 0.71073\text{ \AA}$). Raw data were integrated with the SAINT program^[27]. The structures were solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELX-97 program package^[28, 29]. An empirical absorption correction was applied with the program SADABS. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were set in calculated sites and refined by a riding mode. The crystallographic details of two complexes are provided in Table 1, and the selected bond distances are listed in Tables 2 and 3.

Table1. Crystallographic Data and Structure Refinements for Complexes 1 and 2

Complex	1	2
Empirical formula	C ₈ H ₆ CaO ₈ S	C ₈ H ₆ SrO ₈ S
Formula weight	302.27	349.81
Temperature	296(2) K	296(2) K
Wavelength	0.071073 nm	0.071073 nm
Space group	<i>P</i> 2 ₁ / <i>m</i>	<i>P</i> 2 ₁ / <i>c</i>
Unit cell dimensions	<i>a</i> = 0.82031(8) nm <i>b</i> = 0.68984(7) nm <i>c</i> = 0.94285(9) nm <i>α</i> = 90 ° <i>β</i> = 96.843(3) ° <i>γ</i> = 90 °	<i>a</i> = 1.28856(12) nm <i>b</i> = 0.69449(6) nm <i>c</i> = 1.28856(12) nm <i>α</i> = 90 ° <i>β</i> = 115.50 ° <i>γ</i> = 90 °
Volume	0.52974(9) nm ³	1.04078(16) nm ³
Z, calculated density	2, 1.895 mg/cm ³	4, 2.232 mg/cm ³
Absorption coefficient	0.822 mm ⁻¹	5.414 mm ⁻¹
<i>F</i> (000)	308	688
Theta range for data collection	3.11 to 25.08 °	3.17 to 25.09 °
Reflections collected / unique	1025 / 875	1857 / 1643
Completeness	99.8%	99.9%
<i>GOOF</i>	1.014	1.064
Final <i>R</i> indices (<i>I</i> > 2σ(<i>I</i>))	<i>R</i> = 0.0289 <i>wR</i> = 0.0683	<i>R</i> = 0.0274 <i>wR</i> = 0.0557
<i>R</i> indices (all data)	<i>R</i> = 0.0375 <i>wR</i> = 0.0723	<i>R</i> = 0.0352 <i>wR</i> = 0.0585

Table 2. Selected Bond Lengths (Å) and Bond Angles (°) for 1

Bond	Dist.	Bond	Dist.
Ca(1)–O(2)	2.428(2)	Ca(1)–O(4) ^c	2.331(2)
Ca(1)–O(5)	2.270(2)	Ca(1)–O(4) ^d	2.331(2)
Ca(1)–O(1w)	2.393(2)	Ca(1)–O(3) ^b	2.470(2)
Ca(1)–O(3) ^a	2.470(2)		
Angle	(°)	Angle	(°)
O(5)–Ca(1)–O(4) ^c	98.54(4)	O(5)–Ca(1)–O(3) ^a	96.17(7)
O(5)–Ca(1)–O(4) ^d	98.54(4)	O(4) ^c –Ca(1)–O(3) ^b	74.20(6)
O(4) ^c –Ca(1)–O(4) ^d	152.07(8)	O(4) ^c –Ca(1)– O(3) ^a	125.43(6)

O(5)–Ca(1)–O(1W)	166.47(8)	O(1W)–Ca(1)–O(3) ^a	95.98(6)
O(4) ^c –Ca(1)–O(1W)	79.11(4)	O(2)–Ca(1)–O(3) ^a	153.82(4)
O(4) ^d –Ca(1)–O(1W)	79.11(4)	O(5)–Ca(1)–O(3) ^a	96.17(7)
O(5)–Ca(1)–O(2)	85.96(8)	O(4) ^d –Ca(1)–O(3) ^a	125.43(6)
O(4) ^c –Ca(1)–O(2)	79.67(4)	O(4) ^d –Ca(1)–O(3) ^b	74.20(6)
O(4) ^d –Ca(1)–O(2)	79.67(4)	O(1W)–Ca(1)–O(3) ^a	95.98(6)
O(1W)–Ca(1)–O(2)	80.51(8)	O(2)–Ca(1)–O(3) ^b	153.82(4)

Symmetrical codes: (a) 1+x, y, z; (b) 1+x, 0.5–y, z; (c) 2–x, –y, 1–z; (d) 2–x, 0.5+y, 1–z

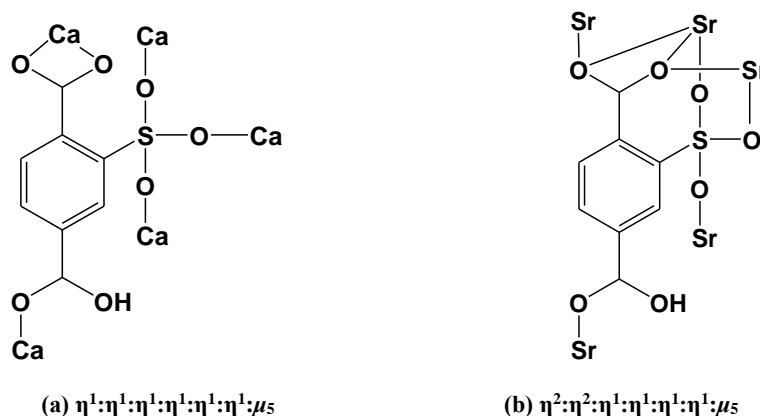
Table 3. Selected Bond Lengths (Å) and Bond Angles (°) for 2

Bond	Dist.	Bond	Dist.
Sr(1)–O(5) ^c	2.523(2)	Sr(1)–O(2) ^a	2.692(2)
Sr(1)–O(7) ^d	2.541(2)	Sr(1)–O(3) ^b	2.708(2)
Sr(1)–O(1)	2.595(2)	Sr(1)–O(4) ^a	2.723(2)
Sr(1)–O(4)	2.608(2)	Sr(1)–O(5) ^a	2.728(2)
Sr(1)–O(1W)	2.689(3)		
Angle	(°)	Angle	(°)
O(5) ^a –Sr(1)–O(7) ^d	87.75(8)	O(1) ^c –Sr(1)–O(3) ^b	132.14(7)
O(5) ^a –Sr(1)–O(1)	76.77(7)	O(4)–Sr(1)–O(3) ^b	131.68(7)
O(7) ^d –Sr(1)–O(1)	75.54(8)	O(1W)–Sr(1)–O(3) ^b	68.39(7)
O(5) ^c –Sr(1)–O(4)	147.53(7)	O(2) ^a –Sr(1)–O(3) ^b	74.13(7)
O(7) ^d –Sr(1)–O(4)	81.71(7)	O(5) ^c –Sr(1)–O(4) ^a	66.62(7)
O(1)–Sr(1)–O(4)	70.88(7)	O(7) ^d –Sr(1)–O(4) ^a	146.26(7)
O(5) ^c –Sr(1)–O(1W)	138.76(7)	O(1)–Sr(1)–O(4) ^a	77.39(7)
O(7) ^d –Sr(1)–O(1W)	73.98(8)	O(4)–Sr(1)–O(4) ^a	107.88(6)
O(1)–Sr(1)–O(1W)	130.49(7)	O(1W)–Sr(1)–O(4) ^a	139.73(7)
O(4)–Sr(1)–O(1W)	66.87(7)	O(2) ^a –Sr(1)–O(4) ^a	67.65(7)
O(5) ^a –Sr(1)–O(2) ^a	95.52(7)	O(3) ^b –Sr(1)–O(4) ^a	117.85(7)
O(7) ^d –Sr(1)–O(2) ^a	139.75(8)	O(5) ^c –Sr(1)–O(5) ^a	114.43(5)
O(1)–Sr(1)–O(2) ^a	144.22(7)	O(7) ^d –Sr(1)–O(5) ^a	145.64(7)
O(4)–Sr(1)–O(2) ^a	112.30(7)	O(1) ^a –Sr(5)–O(3)	84.12(7)
O(1W)–Sr(1)–O(2) ^a	77.57(7)	O(4) ^a –Sr(1)–O(5)	65.42(7)
O(5) ^c –Sr(1)–O(3) ^b	70.61(7)	O(1W)–Sr(1)–O(5) ^a	100.33(7)
O(7) ^d –Sr(1)–O(3) ^b	69.24(7)	O(2) ^a –Sr(1)–O(5) ^a	67.65(7)
O(4) ^a –Sr(1)–O(5) ^a	48.03(7)	O(3) ^d –Sr(1)–O(5) ^a	141.23(7)

Symmetrical codes: (a) 1–x, 0.5+y, 1.5–z; (b) x, 0.5–y, –0.5+z; (c) x, 1+y, z; (d) 2–x, –y, 2–z

3 RESULTS AND DISCUSSION

3.1 Crystal structures



Scheme 1. Coordination modes of 2-Hsp²⁻ in complex **1** (a) and **2** (b)

Single-crystal X-ray diffraction analysis reveals that both complexes **1** and **2** exhibit 3D frameworks. The coordination modes of 2-sulfoterephthalate are shown in Scheme 1. Complex **1** crystallizes in the monoclinic space group $P2_1/m$, while complex **2** in the monoclinic space group $P2_1/c$. IR spectra of the two complexes show two absorption peaks at 3426 cm⁻¹ (for **1**) and 3422 cm⁻¹ (for **2**) due to the presence of water molecules. Peaks at 1560 and 1422 cm⁻¹ for **1** and 1578 and 1420 cm⁻¹ for **2** can be assigned to the asymmetric and symmetric stretching vibrations of the carboxylate group in 2-sulfoterephthalate, and the red-shifts compared to that of the free ligand indicate that the carboxylate oxygen atoms are taking part in coordinating, which is in accordance with the results of structural analysis.

The single-crystal X-ray structural analysis shows that the asymmetric unit of complex **1** consists of one calcium(II) ion, one 2-Hsp²⁻ ligand and one water molecule. As shown in Fig. 1, the calcium(II) ion is in a seven-coordinated, slightly distorted pentagon bipyramidal configuration, with O(1w) and O(5) as the vertex atoms and the other oxygen atoms to form a pentagon (Fig. 1a). Three of the oxygen atoms (O(4c), O(4d) and O(5)) are from sulfonate group, two (O(3a) and O(3b)) from the 1-site carboxylate group, one (O(2)) from 4-site carboxylate group of the 2-Hsp ligand and one (O(1w)) from water molecule. In **1**, the 2-Hsp²⁻ ligand adopts the coordination fashion of $\eta^1:\eta^1:\eta^1:\eta^1:\eta^1:\mu_5$ linking five Ca(II) ions, in which the 1-site carboxylate group is in a chelate mode, 2-site sulfonate group is tridentated and the 4-site protonated carboxylate group is

monodentate (Scheme 1a). The Ca–O bond lengths vary from 2.270(2) to 2.470(2) Å, and the O–Ca–O angles are in the range of 74.20(6)~166.47(8)°, which are all in accordance with those found in the other Ca(II) complexes^[25]. The sulfonate group of 2-Hsp²⁻ ligand connects three calcium ions, resulting in a 1D ladder-like chain along the *b* axis. The 1-site carboxylate group adopts a chelating coordination mode, and further extends the adjacent 1D ladder-like chains into a 2D network (Fig. 2a). The 4- and 1-site carboxylate groups of 2-Hsp²⁻ ligands play a very important role in the construction of a 3D framework (Fig. 2b).

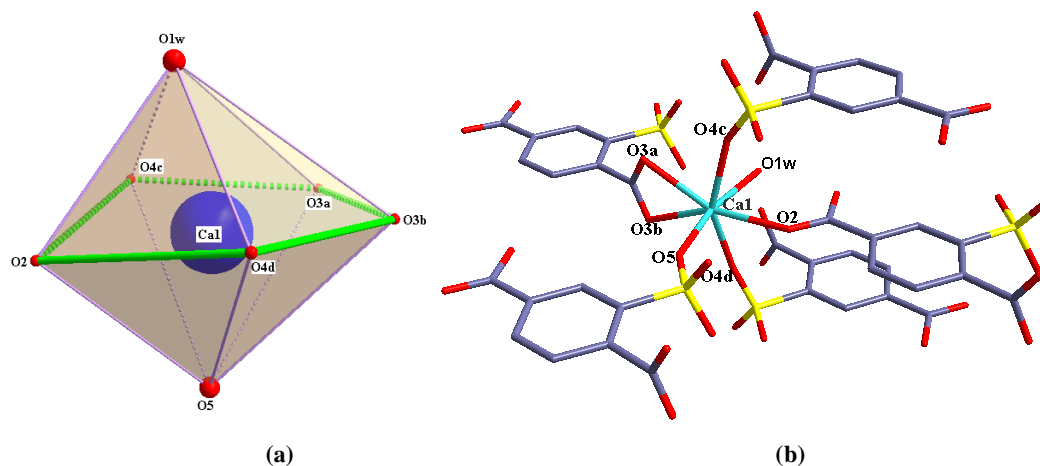


Fig. 1. (a) A pentagon bipyramidal configuration of Ca(II) ion;
(b) Coordination environment of Ca(II) in 1. Hydrogen atoms are omitted for clarity.
Symmetrical codes: (a) 1+x, y, z; (b) 1+x, 0.5-y, z; (c) 2-x, -y, 1-z; (d) 2-x, 0.5+y, 1-z

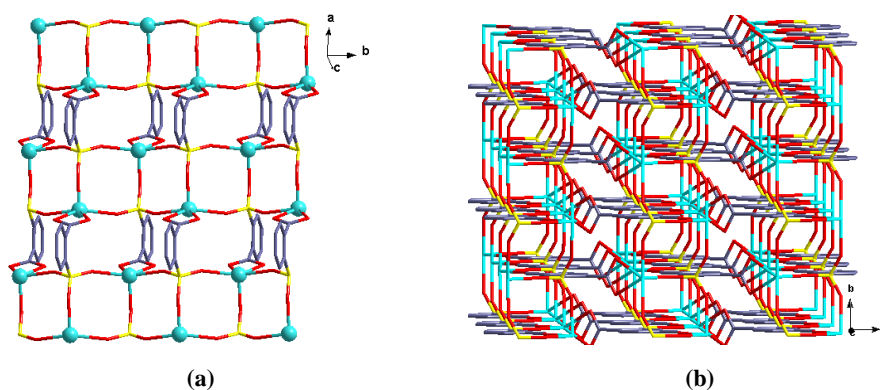


Fig. 2. (a) 2D network in the *ab* plane; (b) 3D framework of complex 1

In complex 2, the asymmetric unit comprises one strontium(II) ion, one 2-Hsp²⁻ anion and one coordinated water molecule. Each Sr(II) is coordinated by nine oxygen atoms, with eight from five 2-Hsp²⁻ ligands and one from the water molecule (Sr–O bond lengths 2.523(2)~2.728(2) Å). Four oxygen atoms (O(4), O(4a), O(5a) and O(5c)) belong to the 1-site carboxylate groups, three (O(1), O(2a) and O(3b)) are from the 2-site

sulfonate groups and O(7d) from the 4-site carboxylate group. The O–Sr–O angles range from 66.62(7) to 147.53(7)°. As illustrated in Fig. 3(a), the Sr(II) ion lies in a distorted single-capped square antiprism geometry, in which O(3b) is the capped atom, and two groups of O(1w), O(2a), O(5c), O(7d) and O(1), O(4), O(4a), O(5) consist of two planes, respectively. The 2-Hstp²⁻ anion adopts a $\eta^2:\eta^2:\eta^1:\eta^1:\eta^1:\eta^1:\mu_5$ coordination mode (Scheme 1b), of which the 1-site carboxylate group links two adjacent Sr(II) ions to form one-dimensional chains along the *b* axis. Then such adjacent chains are further joined and extended into a 2D network via the 2-site sulfonate groups of 2-Hstp²⁻ ligand in the *ab* plane (Fig. 4a). These planes are assembled into a 3D architecture by 4-site carboxylate groups of the ligands (Fig. 4b).

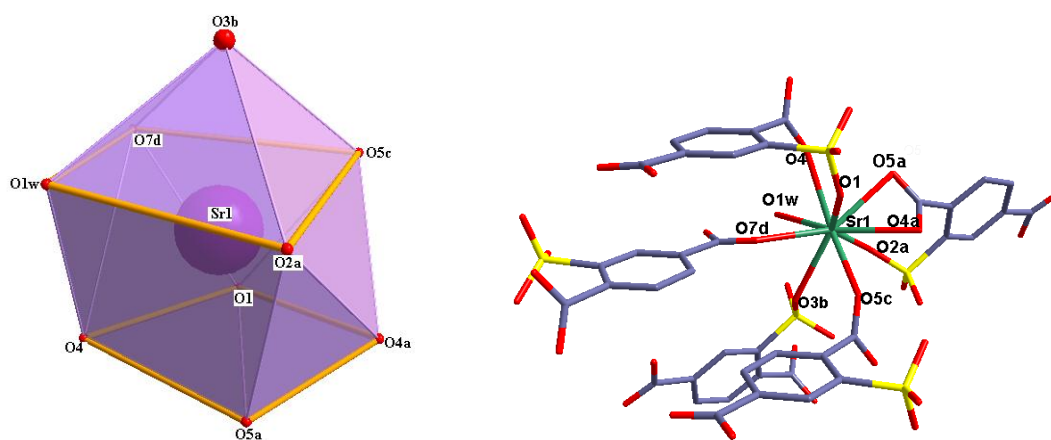


Fig. 3. (a) A single-capped square antiprism configuration of Sr(II) ion;
(b) Coordination environment of Sr(II) in 2. Hydrogen atoms are omitted for clarity.
Symmetrical codes: (a) 1-x, 0.5+y, 1.5-z; (b) x, 0.5-y, -0.5+z; (c) x, 1+y, z; (d) 2-x, -y, 2-z

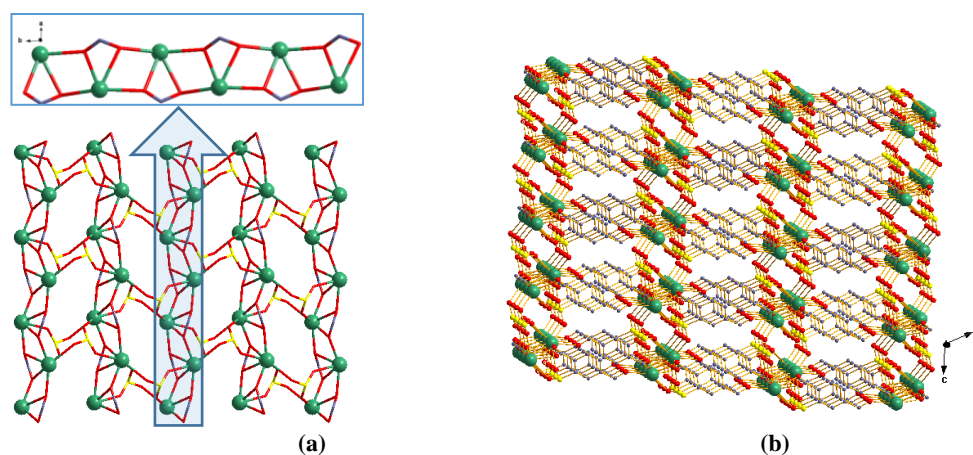


Fig. 4. (a) 2D structure in the *ab* plane featuring 1D chains along the *b* axis; (b) 3D framework of complex 2

3.2 TGA analysis

Thermal gravimetric analyses (TGA) of **1** and **2** are carried out in the temperature range of 25~900 °C in the air with a heating rate of 10 °C min⁻¹ (Fig. 5). For **1**, the first weight loss of 5.90% from 305 to 432 °C could be attributed to the release of one water molecule (calcd. 5.95%), then a big weight loss from 432 to 812 °C could be due to the framework decomposition with the final residue weight to be 40.12%, which might be CaO (calcd. 18.55% based on CaO) and other residues. There are two steps in the TG curve for **2**: the first weight loss is 5.75% (from 294 to 393 °C) probably corresponding to the loss of one water molecule (calcd. 5.15%), then the weight loss from 394 to 760 °C also means the collapse of the whole skeleton of **2**, and probably into SrO with the residue weight of 32.80% (calcd. 29.62% based on SrO).

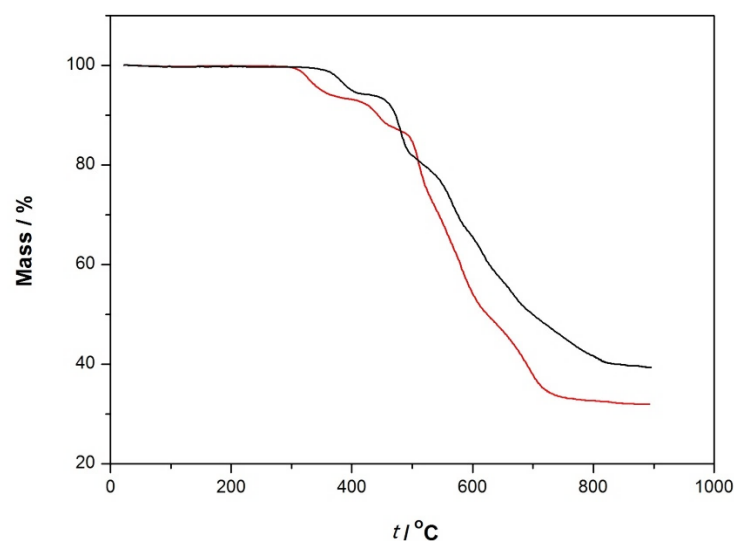


Fig. 5. TGA curves of complexes **1** and **2** (black for complex **1** and red for **2**)

3.3 Powder X-ray diffraction

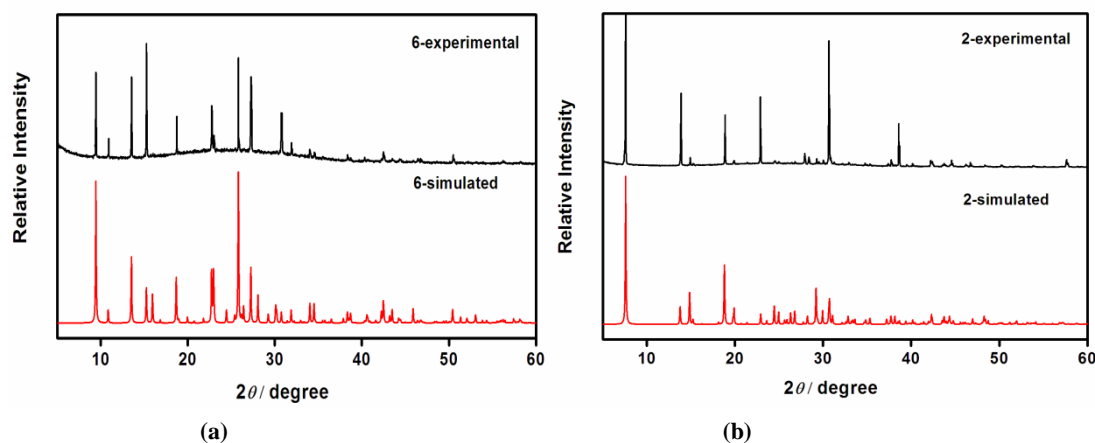


Fig. 6. Experimental and theoretically simulated PXRD patterns for complexes **1** (a) and **2** (b)

From Fig. 6, it can be easily seen that the peak sites of the simulated and experimental powder X-ray diffraction (PXRD) patterns are in good agreement with each other, which indicates high purity of these coordination compounds. The relative intensity deviation between the theoretically simulated and experimental patterns may be due to preferred orientation of the crystalline powder samples.

3.4 Fluorescent properties

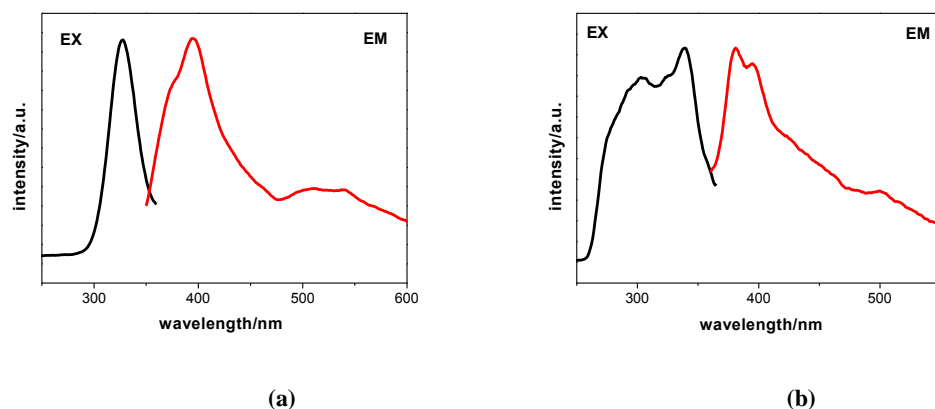


Fig. 7. Excited (black lines) and emission (red lines) curves of complexes 1 (a) and 2 (b)

The fluorescence spectra of complexes **1** and **2** were determined in the solid state at room temperature (Fig. 7) and the free ligand was previously studied^[14]. The emission peaks of complex **1** occur at 405 nm (strong) and 540 nm (weak) upon excitation at 328 nm, which reflect the emission of 2-Hstp²⁻ ligand. In **2**, a similar curve profile of emission spectra is observed, with the maximum emission at 384 and 505 nm upon 340 nm excitation. In regard to the complex of main group elements, the emission associated with electron transition is located predominantly in the organic part of the molecule^[16].

4 CONCLUSION

In summary, the precursor approach enabled us to obtain two new alkaline earth metal (Ca and Sr) coordination polymers based on 2-sulfoterephthalate ligand. They possess similar chemical formulas but different structures for different metal ions. The Ca²⁺ ion of complex **1** is seven-coordinated, while the Sr²⁺ ion lies in a nine-coordinated environment in **2**. The 2-sulfoterephthalate ligand adopts different coordination modes of $\eta^1:\eta^1:\eta^1:\eta^1:\eta^1:\eta^1:\mu_5$ (**1**) and $\eta^2:\eta^2:\eta^1:\eta^1:\eta^1:\eta^1:\mu_5$ (**2**) when constructing the 3D frameworks. The luminescence analysis shows that complexes **1** and **2** exhibit fluorescence in the solid state at room

temperature and may be potential fluorescence materials.

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Crystal Structures, Characterizations and Fluorescence Properties of Two 3D Ca(II)/Sr(II) Coordination Polymers Based on 2-Sulfoterephthalate

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Two alkaline earth metal coordination polymers were synthesized under hydrothermal conditions by a precursor complex and alkaline earth metal salts, which show their structural diversity due to the difference of metal ions. Fluorescence spectra exhibit π - π^* transition of the 2-sulfoterephthalate ligand.

